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## (54) NON-AQUEOUS ELECTROLYTE BATTERY

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery which enables coexistence of high electric discharge capacity and outstanding cycle characteristic, and its manufacturing method by development of a high capacity positive-electrode material which is not accompanied by a generation of gas.

SOLUTION: In a non-aqueous electrolyte battery which consists of a positive- electrode active material which have a compound metal oxide having Li and Ni as main ingredients, a negative electrode which can delete/insert Li, and a non-aqueous electrolyte, the pH of the above compound metal oxide is 10 to 11.5.



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**CLAIMS**

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**[Claim(s)]**

[Claim 1] Said positive active material is a nonaqueous electrolyte cell characterized by being in within the limits whose pH values are 10-11.5 in the nonaqueous electrolyte cell which covered the nonaqueous electrolyte inserted between the positive electrode which contains the multiple oxide which uses Li and nickel as a principal component as positive active material, the negative electrode containing the negative-electrode active material in which storage and emission of Li are possible, and said positive electrode and a negative electrode in the sheathing material, and whose pore pitch diameter is 3-30nm.

[Claim 2] Said positive active material is a nonaqueous electrolyte cell which pH values are 10-11.5 in the nonaqueous electrolyte cell which covered the nonaqueous electrolyte inserted between the positive electrode which contains the multiple oxide which uses Li and nickel as a principal component as positive active material, the negative electrode containing the negative-electrode active material in which storage and emission of Li are possible, and said positive electrode and a negative electrode in the sheathing material, and is characterized by pore volume being within the limits of 0.001 - 0.01 cc/g.

[Claim 3] Said positive active material is claim 1 characterized by being the multiple oxide expressed with (1) type, or a nonaqueous electrolyte cell given in 2.

$\text{Li}_x\text{Ni}_{1-a-b}\text{Co}_a\text{Al}_b\text{O}_2$  (1)

(However,  $0.05 \leq x \leq 1.10$ ,  $0.15 \leq a \leq 0.25$ ,  $0 < b \leq 0.10$ )

[Claim 4] Said sheathing material is claim 1 characterized by consisting of a sheet with a thickness of 0.5mm or less, or a nonaqueous electrolyte cell given in two.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a nonaqueous electrolyte cell.

[0002]

[Description of the Prior Art] The lithium secondary battery is commercialized as a nonaqueous electrolyte rechargeable battery for pocket devices, such as current and a cellular phone. The organic solvent with which this cell dissolved the graphite ingredient and the carbonaceous ingredient in lithium cobalt oxide ( $\text{LiCoO}_2$ ) and a negative electrode, and dissolved lithium salt in nonaqueous electrolyte at the positive electrode is used.[0003] However, with multi-functionalization and high-performance-izing of a pocket device, the power consumption of a device is increasing and the demand of high-capacity-izing is becoming still stronger to the cell used as the power source in recent years. Then, compared with conventional lithium cobalt oxide, development of the lithium nickel oxide ( $\text{LiNiO}_2$  and  $\text{Li}_{1-x}\text{Ni}_x\text{Co}_{1-y}\text{Al}_y\text{O}_2$ ) which can expect high capacity-ization is progressing (JP,2000-195514,A etc.).[0004] Moreover, on the other hand, light weight and thin shape-ization of a pocket device takes for progressing, thin shape-ization of the cell itself is also needed, development of the thin cell which uses a laminate film as a sheathing material recently also progresses, and the thin cell using the organic solvent and polymer electrolyte which dissolved the graphite ingredient and the carbonaceous ingredient in lithium cobalt oxide ( $\text{LiCoO}_2$ ) and a negative electrode, and dissolved lithium salt in the positive electrode at nonaqueous electrolyte is being put in practical use.

[0005] However, when this lithium nickel oxide was used for the lamination type thin cell, a lot of gas occurred at the time of an initial charge and elevated-temperature storage, and the problem that a cell will blister greatly had arisen.

[0006]

[Problem(s) to be Solved by the Invention] This invention was made in order to solve the above-mentioned conventional trouble, it is excellent in the charge-and-discharge cycle engine performance with high capacity, and tends to offer the nonaqueous electrolyte cell which excelled [ high capacity ] in the cycle life by using the positive electrode which gas cannot generate easily at the time of an initial charge or elevated-temperature storage.

[0007]

[Means for Solving the Problem] In the nonaqueous electrolyte cell which covered the nonaqueous electrolyte inserted between the positive electrode which contains the multiple oxide with which the nonaqueous electrolyte cell of this invention uses Li and nickel as a principal component as positive active material, the negative electrode containing the negative-electrode active material in which storage and emission of Li are possible, and said positive electrode and a negative electrode in the sheathing material, pH values are 10-11.5 and said positive active material is characterized by being in within the limits whose pore pitch diameter is 3-30nm.

[0008] In the nonaqueous electrolyte cell which covered the nonaqueous electrolyte inserted between the positive electrode which contains the multiple oxide with which the nonaqueous electrolyte cell of this invention uses Li and nickel as a principal component as positive active material, the negative electrode containing the negative-electrode active material in which storage and emission of Li are possible, and said positive electrode and a negative electrode in the sheathing material, pH values are 10-11.5 and said positive

active material is characterized by pore volume being within the limits of 0.001 - 0.01 cc/g.

[0009] Moreover, the multiple oxide expressed with (1) type can be used for said positive active material.

[0010]

$\text{Li}_x\text{Ni}_{1-a-b}\text{Co}_a\text{Al}_b\text{O}_2$  (1)

(However,  $0.05 \leq x \leq 1.10$ ,  $0.15 \leq a \leq 0.25$ ,  $0 < b \leq 0.10$ )

Moreover, said sheathing material can use a sheet with a thickness of 0.5mm or less.

[0011]

[Embodiment of the Invention] The thin rechargeable lithium-ion battery which is an example of the nonaqueous electrolyte rechargeable battery of this invention is explained to a detail with reference to drawing 1 thru/or drawing 3. The sectional view showing the thin rechargeable lithium-ion battery whose drawing 1 is an example of the 1st [concerning this invention] nonaqueous electrolyte rechargeable battery, the expanded sectional view in which drawing 2 shows the A section of drawing 1, and drawing 3 are the mimetic diagrams showing the separator of the positive-electrode layer in the rechargeable battery of drawing 1, and porosity nature, and near the boundary of a negative-electrode layer.

[0012] As shown in drawing 1, the sheathing material 1 which consists of a film is surrounding the electrode group 2. Said electrode group 2 has the structure where the laminated material which consists of a positive electrode, a separator, and a negative electrode was wound around the flat configuration.

[0013] As shown in drawing 2, a separator 3, a positive electrode 12, a separator 3, a negative electrode 13, the separator 3, the positive electrode 12, the separator 3, and the negative electrode 13 carried out the laminating of the laminated material one by one (from the drawing bottom). A positive electrode 12 pinches the positive-electrode charge collector 5 in the positive-electrode layer 4 of a pair, and a negative electrode 13 is the structure which pinched the negative-electrode charge collector 7 in the negative-electrode layer 6 of a pair.

[0014] Said negative-electrode charge collector 7 is located in the outermost layer, as for the front face of this electrode group 2, jointing 8 exists, and the electrode group 2 has pasted up the inside of a sheathing material 1 on the electrode group 2 by said jointing 8.

[0015] In such a thin rechargeable lithium-ion battery, the positive-electrode layer 4 or the negative-electrode layer 6 is arranged at the front flesh side of a separator 3. Between the particles which constitute the positive-electrode layer 4 or the negative-electrode layer 6 as shown in drawing 3, this particle, and the macromolecule 9 that has an adhesive property in the opening of a separator 3 are held, respectively. The positive electrode 12 and the separator 3 are pasted up with the macromolecule 9 which has the adhesive property with which the interior and these boundaries of the positive-electrode layer 4 and a separator 3 are dotted. On the other hand, the negative electrode 13 and the separator 3 are pasted up with the macromolecule 9 which has the adhesive property with which the interior and these boundaries of the negative-electrode layer 6 and a separator 3 are dotted.

[0016] For example, nonaqueous electrolyte is infiltrated into the electrode group 2 in said sheathing material 1, and a separator is operated as an electrolyte plate by supplying into the pore of a separator.

[0017] The end of the band-like positive-electrode lead 10 is connected to the positive-electrode charge collector 5 of the electrode group 2, and on the other hand, the other end of the positive-electrode lead 10 is made to extend from a sheathing material 1, and is connected with a positive-electrode terminal. Moreover, the end of the negative-electrode lead 11 is connected to the negative-electrode charge collector 7 of the electrode group 2, and the other end extends from a sheathing material 1, and is connected with a negative-electrode terminal. In addition, in drawing 1 mentioned above, although jointing 8 was formed in the whole front face of the electrode group 2, jointing 8 may be formed in a part of electrode group 2. When forming jointing 8 in a part of electrode group 2, it is desirable to form in the field which is equivalent to the outermost periphery of an electrode group at least. Moreover, there may not be jointing 8.

[0018] Hereafter, a positive electrode 12, a negative electrode 13, a separator 3, etc. are explained to a detail for every configuration.

[0019] 1) Positive-electrode 12 positive electrode is having structure in which the positive-electrode layer was formed to one side or both sides of a charge collector. This positive-electrode layer may contain at least the binder which binds positive active material, including positive active material and an electric conduction agent.

[0020] The positive active material concerning this invention is a multiple oxide which uses Li and nickel as a principal component (it is hereafter called nickel system active material). This nickel system active material can

enlarge cell capacity compared with the cell which used  $\text{LiCoO}_2$  etc.

[0021] A multiple oxide as shown in a formula (1) can more specifically be used, and the thing which is illustrated here and which permuted like and nickel part by other elements, such as Co and aluminum, can be used.

[0022]

$\text{Li}_x\text{Ni}_{1-a-b}\text{Co}_a\text{Al}_b\text{O}_2$  (1)

However, in x in a formula (1), a fills  $0.15 \leq a \leq 0.25$ , and b fills  $0 < b \leq 0.10$  for  $0.05 \leq x \leq 1.10$ .

[0023] Moreover, as for this nickel system active material used for this invention, that pH value is controlled within the limits of 10-11.5. The reason is explained below.

[0024] In nickel system active material production process, in case a lithium carbonate makes a lithium hydroxide and a nickel hydroxide (the hydroxide of a nickel alloy is also included) react in an oxygen ambient atmosphere, it originates in Li component which was not able to turn completely into a multiple oxide, and is sub\*(ed). When this amount of lithium carbonates is reduced and a pH value shows, it becomes possible to control the amount of generation of gas by making it smaller than 11.5.

[0025] Although this reason is not certain, since a carbon dioxide and hydrocarbon gas occur at the lithium carbonate which remains on an active material front face reacting with the electrolytic solution etc., if nickel system active material is used by reducing the amount of survival of this lithium carbonate, I will think that the capacity generated at the time of an initial charge and elevated-temperature storage has been reduced.

[0026] Moreover, although it is possible to reduce the amount of lithium carbonates which subgenerates the ratio of a lithium hydroxide by lessening, and to reduce a pH value when [ of a lithium hydroxide and a nickel hydroxide ] making it react, the ratio of the lithium in the active material which will be obtained if the ratio of a lithium hydroxide is reduced falls, and, as a result, cell capacity falls. Therefore, in order not to reduce the amount of lithium hydroxides used in order to hold cell capacity to high capacity, the pH value of the active material obtained becomes larger than 10.

[0027] Moreover, it is desirable that the range of the pH value of positive active material is 10.5-11.25 more preferably in consideration of maintenance of cell capacity and reduction of the amount of generation of gas.

[0028] In addition, pH of the positive active material concerning this invention is measured in the following procedures. That is, an active material is filtered and filtrate is obtained, after distributing 2g to 100ml pure water and agitating positive active material for about 10 minutes. pH of this filtrate is set to pH of positive active material.

[0029] moreover, this invention persons have the pore diameter whose 80% or more of the pore volume is 1nm - 100nm in the positive active material concerning this invention which was mentioned above -- or -- and by using the particle in within the limits which is 3-30nm, since it fully sank into positive active material, it was hard to change into the overcharge condition, and the pore pitch diameter found out that the electrolytic solution is smooth and that the generation of gas could be controlled effectively. That is, if a pore diameter is smaller than 1nm, sinking [ of the electrolytic solution ] in will not be smoothly performed for physical resistance, but if larger than 100nm, it will sink in in respect of the wettability of the electrolytic solution, or capillarity, and will become hot. Moreover, as for the same viewpoint to pore volume, it is desirable that it is within the limits of 0.001 - 0.01 cc/g. The amounts of electrolytic solutions which will sink in if pore volume is smaller than 0.001 cc/g run short, and generation-of-gas depressor effect fades. Generation-of-gas depressor effect increases so that pore volume becomes large, but since the increment in the volume leads to the fall of the energy density per volume, considering as 0.01 or less cc/g is desirable.

[0030] Furthermore, as for the presentation of the viewpoint of capacity and cycle nature to said multiple oxide, it is desirable to control within the limits of (1) type, and it is desirable to control within the limits of (2) types further.

[0031]

$\text{Li}_x\text{Ni}_{1-a-b}\text{Co}_a\text{Al}_b\text{O}_2$  (2)

(However,  $0.05 \leq x \leq 1.10$ ,  $0.18 \leq a \leq 0.20$ ,  $0.03 \leq b \leq 0.07$ )

Moreover, the positive active material concerning this invention is the following, and can be made and produced.

[0032] Although a lithium hydroxide and a nickel hydroxide are used as a raw material The description of these raw material complications is important, and a raw material with a large specific surface area is used, It is

desirable to use the small thing of the particle size distribution of raw material powder, for example, it is about 0.1-3 micrometers in mean particle diameter more preferably using specific-surface-area the thing which is about 2/g of 10-100m, and the mean particle diameter of 10 micrometers or less. It is desirable to use the ingredient which has the path of the particle beyond 80wt% in \*\*20% of range of mean particle diameter. Moreover, it is desirable that the ratios of the mean particle diameter of lithium-hydroxide raw material powder and nickel hydroxide raw material powder are 0.8-1.2.

[0033] Thus, when the grain size and specific surface area of a raw material were controlled and grinding mixing is carried out with a distributed vessel by using an organic solvent as a solvent, a raw material can make the condition of having distributed to a detail and homogeneity, and smooth baking of it is attained at the following processes. That is, the amount of generation of the lithium carbonate which is a by-product can be reduced more.

[0034] After drying to homogeneity the raw material mixed and distributed, temporary baking around 500 degrees C and this baking around 750 degrees C are performed. although firing time comes out enough in about 10 - 50 hours -- an oxidizing atmosphere -- the inside of an oxygen air current needs to be calcinated preferably. Although this condition is a well-known technique, it is desirable to calcinate in this invention under the pressure from which the inside of a baking chamber does not become negative pressure. Thereby, scattering of a lithium hydroxide decreases and positive active material with few lithium-carbonate contents sub\*\*(ed) can be obtained.

[0035] Moreover, as for baking mentioned above, it is desirable to pelletize the mixed raw material powder beforehand. Although it is not limited, when the ease of carrying out and handling nature of grinding after composition are taken into consideration, as for especially the size of a pellet, it is desirable to make it the size of diameter extent of 5-30mm. By doing in this way, even if it manufactures positive active material with comparatively many lithium element components, while becoming possible to reduce the amount of lithium carbonates subgenerated at the time of baking, an average pole diameter can obtain the positive active material with which pore capacity was controlled by 3-30nm by 0.001 - 0.1 cc/g.

[0036] As said electric conduction agent, acetylene black, carbon black, a graphite, etc. can be mentioned, for example. Said binder has the function which is made to hold an active material to a charge collector, and connects active materials. As said binder, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), an ethylene-propylene-diene copolymer (EPDM), a styrene butadiene rubber (SBR), etc. can be used, for example.

[0037] the blending ratio of coal of said positive active material, an electric conduction agent, and a binder -- 80 - 95 % of the weight of positive active material, and an electric conduction agent -- it is desirable to make it the range of 2 - 7 % of the weight of binders three to 20% of the weight.

[0038] As said charge collector, the conductive substrate of a vesicular structure or a nonporous conductive substrate can be used. These conductivity substrate can be formed from aluminum, stainless steel, or nickel.

[0039] It is desirable to use the conductive substrate which has the two-dimensional vesicular structure in which 10cm of holes with a diameter of 3mm or less exists at a rate of one or more per two especially. That is, when the diameter of the hole by which opening was carried out to the conductive substrate becomes larger than 3mm, there is a possibility that sufficient positive-electrode reinforcement may no longer be obtained. On the other hand, if the abundance of a hole with a diameter of 3mm or less becomes less than said range, since it will become difficult to make nonaqueous electrolyte permeate homogeneity at an electrode group, there is a possibility that sufficient charge-and-discharge cycle property may no longer be acquired. As for the diameter of a hole, it is more desirable to make it the range of 0.1-1mm. Moreover, as for the abundance of a hole, it is more desirable that 10-20 range per two costs 10cm.

[0040] As for the conductive substrate which has the two-dimensional vesicular structure in which 10cm of holes with a diameter of 3mm or less mentioned above exists at a rate of one or more per two, it is desirable to make thickness into the range of 10-100 micrometers. When thickness is set to less than 10 micrometers, there is a possibility that sufficient positive-electrode reinforcement may no longer be obtained. On the other hand, when thickness exceeds 100 micrometers, the thickness of cell weight and an electrode group increases, and there is a possibility that it may become difficult to make high enough the weight energy density and volume energy density of a thin rechargeable battery. The more desirable range of thickness is 12-50 micrometers.

[0041] A nonporous conductive substrate can also be used as said charge collector. As for the thickness of a charge collector, at this time, it is desirable to make it the range of 5-20 micrometers. It is because positive-

electrode reinforcement and lightweight-izing can be balanced as it is this within the limits.

[0042] As for the thickness of a positive-electrode layer, it is desirable to make it the range of 10-100 micrometers. In addition, when the positive-electrode layer is supported by both sides of a positive-electrode charge collector, the thickness of one side of a positive-electrode layer serves as range whose sum total thickness of a positive-electrode layer is 20-200 micrometers by 10-100 micrometers. If thickness of a positive-electrode layer is set to less than 10 micrometers, since the rate of a current collection weight quantitative ratio and the rate of a volume ratio will become high, energy density falls. The lower limit with desirable thickness is 30 micrometers, and a still more desirable lower limit is 50 micrometers. On the other hand, if the thickness of a positive-electrode layer exceeds 100 micrometers, since nonaqueous electrolyte will concentrate on a positive-electrode front face at the time of a rapid charge-and-discharge cycle and the electrode reaction in the interior of a positive electrode will hardly advance, a cycle life falls. The upper limit with desirable thickness is 85 micrometers, and a still more desirable upper limit is 60 micrometers. As for especially the thickness of a positive-active-material layer, it is desirable to make it the range of 10-60 micrometers. A high current discharge property and a cycle life improve sharply that it is this within the limits. Furthermore, the desirable range is 30-50 micrometers. The thickness of said positive-electrode layer is measured by the approach explained below. First, mutually, it separates 1cm or more, and ten existing points are chosen as arbitration, the thickness of each point is measured, and the thickness of a positive electrode is measured by computing the average. However, when the positive electrode which it is going to measure has the structure where the positive-active-material layer was supported by both sides of a charge collector, after removing positive-active-material layer of one of the two, the thickness of a positive electrode is measured. Subsequently, a positive-active-material layer is removed from a charge collector, and the thickness of a charge collector is measured. The thickness of a charge collector chooses as arbitration ten points which separate 1cm or more and exist mutually, measures the thickness of each point, and is called for by computing the average. Let the difference of the thickness of said positive electrode, and the thickness of said charge collector be the thickness of the positive-active-material layer for which it asks. As for the voidage of a positive-electrode layer, it is desirable to make it low compared with the voidage of a negative-electrode layer. Moreover, as for the voidage of a positive-electrode layer, it is desirable to make it 25 - 40% of range. This is based on the following reasons. When voidage is made less than 25%, even if it has regulated the thickness of a positive-electrode layer, there is a possibility that it may become difficult to make nonaqueous electrolyte permeate homogeneity. On the other hand, when voidage exceeds 40%, there is a possibility that it may become impossible to obtain high capacity, i.e., a high energy consistency. The more desirable range of voidage is 30 - 35%.

[0043] 2) A negative-electrode negative electrode has the structure where the negative-electrode layer containing the macromolecule and binder which have negative-electrode active materials, such as occlusion and a carbonaceous object to emit, and an adhesive property for a lithium ion was supported by one side or both sides of a negative-electrode charge collector.

[0044] Said negative-electrode layer contains occlusion and the negative-electrode active material to emit for a lithium ion. Moreover, the negative-electrode layer contains the binder which binds a negative-electrode ingredient apart from the macromolecule which has an adhesive property. A graphite ingredient or a carbonaceous ingredient obtained as said carbonaceous object by heat-treating at 500-3000 degrees C to graphite ingredients, such as a graphite, corks, a carbon fiber, and spherical carbon, or a carbonaceous ingredient, thermosetting resin, an isotropic pitch, a mesophase pitch, a mesophase pitch based carbon fiber, a mesophase microsphere, etc. (a mesophase pitch based carbon fiber becoming high and having capacity and an especially desirable charge-and-discharge cycle property) can be mentioned. Especially, it is obtained by making temperature of said heat treatment into 2000 degrees C or more, and it is desirable to use the graphite ingredient which has the graphite crystal whose spacing d002 of a field (002) is 0.340nm or less. The nonaqueous electrolyte rechargeable battery equipped with the negative electrode which contains such a graphite ingredient as a carbonaceous object can improve sharply cell capacity and a high current discharge property. As for said spacing d002, it is still more desirable that it is 0.336nm or less.

[0045] As said binder, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), an ethylene-propylene-diene copolymer (EPDM), styrene-PUTAJI en rubber (SBR), a carboxymethyl cellulose (CMC), etc. can be used, for example.

[0046] As for the blending ratio of coal of a carbonaceous object and said binder, it is desirable that it is the

range of 90 - 98 % of the weight of carbonaceous objects and 2 - 20 % of the weight of binders.

[0047] As a negative-electrode charge collector, the conductive substrate of a vesicular structure or a nonporous conductive substrate can be used. These conductivity substrate can be formed from copper, stainless steel, or nickel.

[0048] It is desirable to use the conductive substrate which has the two-dimensional vesicular structure in which 10cm of holes with a diameter of 3mm or less exists at a rate of one or more per two especially. That is, when the diameter of the hole of a conductive substrate becomes larger than 3mm, there is a possibility that sufficient negative-electrode reinforcement may no longer be obtained. On the other hand, if the abundance of a hole with a diameter of 3mm or less becomes less than said range, since it will become difficult to make nonaqueous electrolyte permeate homogeneity at an electrode group, there is a possibility that sufficient charge-and-discharge cycle property may no longer be acquired. As for the diameter of a hole, it is more desirable to make it the range of 0.1-1mm. Moreover, as for the abundance of a hole, it is more desirable that 10-20 range per two costs 10cm.

[0049] As for the conductive substrate which has the two-dimensional vesicular structure in which 10cm of holes with a diameter of 3mm or less mentioned above exists at a rate of one or more per two, it is desirable to make thickness into the range of 8-50 micrometers. When thickness is set to less than 8 micrometers, there is a possibility that sufficient negative-electrode reinforcement may no longer be obtained. On the other hand, when thickness exceeds 50 micrometers, the thickness of cell weight and an electrode group increases, and there is a possibility that it may become difficult to make high enough the weight energy density and volume energy density of a thin rechargeable battery.

[0050] A nonporous conductive substrate can also be used as a negative-electrode charge collector. As for the thickness of a charge collector, at this time, it is desirable to make it the range of 5-20 micrometers. It is because negative-electrode reinforcement and lightweight-izing can be balanced as it is this within the limits.

[0051] especially if negative-electrode layers are occlusion and matter to emit, they will restrict a lithium ion -- not having -- except for the carbon matter -- metals, such as aluminum, magnesium, tin, and a silicon, a metallic oxide, and metallic sulfide -- or the metallic compounds chosen from a metal nitride and a lithium alloy may be included.

[0052] As said metallic oxide, a stannic-acid ghost, silicon oxide, a lithium titanate-acid ghost, a niobic acid ghost, a tungstic-acid ghost, etc. can be mentioned, for example. As said metallic sulfide, a tin sulfide, a titanium sulfide, etc. can be mentioned, for example.

[0053] As said metal nitride, a lithium cobalt nitride, a lithium iron nitride, a lithium manganese nitride, etc. can be mentioned, for example.

[0054] As said lithium alloy, a lithium aluminium alloy, a lithium tin alloy, a lithium lead alloy, a lithium silicon alloy, etc. can be mentioned, for example.

[0055] As for the thickness of a negative-electrode layer, it is desirable to make it the range of 10-100 micrometers. In addition, when the negative-electrode active material layer is supported by both sides of a negative-electrode charge collector, it is desirable to set thickness of one side of a negative-electrode active material layer to 10-100 micrometers, and to make sum total thickness of a negative-electrode active material layer into the range of 20-200 micrometers. If thickness of a negative-electrode active material layer is set to less than 10 micrometers, since the rate of a current collection weight quantitative ratio and the rate of a volume ratio will become high, there is a possibility that it may become difficult to fully raise energy density. The lower limit with desirable thickness is 30 micrometers, and a still more desirable lower limit is 50 micrometers. On the other hand, if the thickness of a negative-electrode active material layer exceeds 100 micrometers, since it will become easy to concentrate nonaqueous electrolyte on a negative-electrode front face, there is a possibility that it may become difficult to fully improve a cycle life. The upper limit with desirable thickness is 85 micrometers, and a still more desirable upper limit is 60 micrometers. As for especially the thickness of a negative-electrode active material layer, it is desirable to make it the range of 10-60 micrometers. A high current discharge property and a cycle life improve sharply that it is this within the limits. Furthermore, the desirable range is 30-50 micrometers.

[0056] The thickness of a negative-electrode layer can be measured like the thickness of a positive-electrode layer.

[0057] As for the voidage of said negative-electrode active material layer, it is desirable to make it 35 - 50% of



range. This is based on the following reasons. Since there is a possibility that distribution of nonaqueous electrolyte may become an ununiformity when voidage is made less than 35%, lithium DIN DORAIDO may deposit. On the other hand, when voidage exceeds 50%, there is a possibility that it may become impossible to obtain high capacity, i.e., a high energy consistency. The more desirable range of voidage is 35 - 45%.

[0058] As for the blending ratio of coal of a negative-electrode active material and said binder, it is desirable that it is the range of 90 - 98 % of the weight of negative-electrode active materials and 2 - 20 % of the weight of binders. Said especially carbonaceous object is 10 - 70 g/cm<sup>2</sup> at one side, where a negative electrode is produced. It is desirable to make it the range. The consistency of said negative-electrode layer is 1.20 - 1.50 g/cm<sup>3</sup>. It is desirable to make it the range.

[0059] 3) A separator separator has the function into which between a positive electrode and a negative electrode is made to divide electrically, and a function as an electrolyte plate, and an insulating porosity sheet is used.

[0060] For example, it is desirable to be able to use a porosity film or a nonwoven fabric and to consist of at least one kind of ingredient chosen from polyolefine and a cellulose as the quality of the material, for example.

[0061] As polyolefine, polyethylene and polypropylene can be mentioned, for example. Since the porosity film which consists of polyethylene, polypropylene, or both especially can improve the safety of a rechargeable battery, it is desirable. As for the thickness of a separator, it is desirable to make it 30 micrometers or less. When thickness exceeds 30 micrometers, there is a possibility that the distance between forward negative electrodes may become large, and internal resistance may become large. Moreover, as for the lower limit of thickness, it is desirable to make it 5 micrometers. When thickness is set to less than 5 micrometers, the reinforcement of a separator falls remarkably and there is a possibility of becoming easy to produce internal short-circuit. As for the upper limit of thickness, it is more desirable to make it 25 micrometers, and, as for a lower limit, it is more desirable to make it 10 micrometers.

[0062] As for a separator, it is desirable that it is 20% or less about \*\*, 120 degrees C, and the rate of a heat shrink in 1 hour. When said rate of a heat shrink exceeds 20%, there is a possibility that it may become difficult to make bond strength of a forward negative electrode and a separator into sufficient thing. As for said rate of a heat shrink, it is more desirable to make it to 15% or less.

[0063] Although a porous sheet is used in order to operate a separator as an electrolyte plate, it is desirable that it is the range whose porosity is 30 - 60%. When porosity is made less than 30%, there is a possibility that it may become difficult to acquire high electrolytic-solution holdout in a separator. On the other hand, when porosity exceeds 60%, there is a possibility that it may become impossible to obtain sufficient separator reinforcement. The more desirable range of porosity is 35 - 50%.

[0064] As for a separator, it is desirable that air permeability is or less [ 100cm ] 600 seconds / 3. Air permeability means the time amount (second) taken for the air of 3 to penetrate a porosity sheet 100cm. There is a possibility that it may become [ air transmission ] difficult 600 seconds / to obtain high lithium ion mobility in a separator if 3 is exceeded 100cm. Moreover, it is desirable 100 seconds / to set to 3 100cm the lower limit of air permeability. It is because there is a possibility that it may become impossible to obtain sufficient separator reinforcement when air permeability is made into less than [ 100cm ] 100 seconds / 3. The upper limits with more desirable still more desirable [ the upper limit of air permeability ] 500 seconds / 3 costing 100cm are 400 second / 100cm<sup>3</sup>. Moreover, it is more desirable 150 seconds / to set to 3 100cm a lower limit.

[0065] Next, the nonaqueous electrolyte held in a separator is explained.

[0066] It dissolves into a non-aqueous solvent and an electrolyte is held in a separator as the electrolytic solution. Although nonaqueous electrolyte is mainly hereafter explained as nonaqueous electrolyte, if the gel object which is not restricted to a liquid configuration and contained the non-aqueous solvent and the electrolyte in polymeric materials, the solid-state-like object which made the solid-state giant molecule contain an electrolyte have lithium ion conductivity, as for especially this, it bases on the condition and is usable.

[0067] As nonaqueous electrolyte, lithium salt can be dissolved in the non-aqueous solvent of a lithium cell as an electrolyte, a well-known non-aqueous solvent can be used as a solvent component, and it is more desirable than annular carbonate, such as ethylene carbonate (EC) and propylene carbonate (PC), and annular carbonate and annular carbonate to use the non-aqueous solvent which makes a subject a mixed solvent with the non-aqueous solvent (the following 2nd solvent) of hypoviscosity. As the 2nd solvent, dimethoxyethane, diethoxy ethane, etc. are mentioned as the chain-like ether, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, for

example as chain-like carbonate, such as dimethyl carbonate, methylethyl carbonate, and diethyl carbonate, gamma-butyrolactone, an acetonitrile, methyl propionate, ethyl propionate, and cyclic ether.

[0068] As an electrolyte, although alkali salt is mentioned, especially lithium salt is mentioned. As lithium salt, a 6 phosphorus-fluoride acid lithium ( $\text{LiPF}_6$ ), hexafluoroborate lithium ( $\text{LiBF}_4$ ), a 6 arsenic-fluoride lithium ( $\text{LiAsF}_6$ ), lithium perchlorate ( $\text{LiClO}_4$ ), a trifluoro meta-sulfonic-acid lithium ( $\text{LiCF}_3\text{SO}_3$ ), etc. are mentioned. Especially, a 6 phosphorus-fluoride acid lithium ( $\text{LiPF}_6$ ) and hexafluoroborate lithium ( $\text{LiBF}_4$ ) are desirable. As for the amount of dissolutions to said non-aqueous solvent of said electrolyte, it is desirable to carry out in 0.5-2.0 mols/l.

[0069] It is what dissolved said solvent and said electrolyte in polymeric materials as a gel electrolyte, and was made into gel, and the polymer of monomers, such as a polyacrylonitrile, polyacrylate, polyvinylidene fluoride (PVdF), and polyethylene oxide (PEO), or a copolymer with other monomers is mentioned as polymeric materials.

[0070] As a solid electrolyte, it dissolves in polymeric materials and said electrolyte is solidified. As polymeric materials, the polymer of monomers, such as a polyacrylonitrile, polyvinylidene fluoride (PVdF), and polyethylene oxide (PEO), or a copolymer with other monomers is mentioned. Moreover, the ceramic ingredient containing a lithium is mentioned as an inorganic solid electrolyte.  $\text{Li}_3\text{N}$  and  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  glass etc. is mentioned especially.

[0071] It is desirable to use the electrolytic solution which made the subject gamma-butyl lactone (BL) shown below in the case of a thin rechargeable battery. The electrolytic solution is what dissolved lithium salt in the mixed non-aqueous solvent which makes gamma-butyrolactone (BL) a subject, and there are more presentation ratios of BL than 50 volume % of the mixed whole non-aqueous solvent, and they are below 95 volume %. It is become easy to generate gas at the time of an elevated temperature that a ratio is below 50 volume %.

Moreover, since the ratio of annular carbonate becomes high relatively when a mixed non-aqueous solvent is a thing containing BL and annular carbonate, solvent viscosity becomes high and the conductivity of nonaqueous electrolyte falls. Consequently, a charge-and-discharge cycle property, a high current discharge property, and the discharge property under the low-temperature environment near  $-20^\circ\text{C}$  fall. On the other hand, if a ratio exceeds 95 volume %, since the reaction of a negative electrode and BL will arise, a charge-and-discharge cycle property falls. That is, if a negative electrode (for example, thing containing the carbonaceous object which carries out occlusion emission of the lithium ion), and BL react and reduction decomposition of nonaqueous electrolyte arises, the coat which checks a charge-and-discharge reaction on the surface of a negative electrode will be formed. Consequently, since it becomes easy to produce current concentration in a negative electrode, a lithium metal deposits, or the impedance of a negative-electrode interface becomes high, the charge-and-discharge effectiveness of a negative electrode falls to a negative-electrode front face, and the fall of a charge-and-discharge cycle property is caused. The more desirable range is below 95 volume % more than 60 volume %. While being able to make higher effectiveness which controls the generation of gas at the time of elevated-temperature storage by making it this range, the discharge capacity under the low-temperature environment near  $-20^\circ\text{C}$  can be improved more. Furthermore, the desirable range is below 90 volume % more than 65 volume %.

[0072] As a solvent mixed with BL, it is desirable at the point that annular carbonate raises the charge-and-discharge effectiveness of a negative electrode.

[0073] As said annular carbonate, (propylene carbonate PC) (ethylene carbonate EC) (vinylene carbonate VC) trifluoromethyl propylene carbonate (TFPC) etc. is desirable. If EC is used as a solvent especially mixed with BL, a charge-and-discharge cycle property and a high current discharge property can be improved sharply. Moreover, it is desirable at the point which raises a charge-and-discharge cycle property as it is the mixed solvent of the 3rd solvent and EC which are chosen from the group which consists of PC, VC, TFPC, diethyl carbonate (DEC), methylethyl carbonate (MEC), and an aromatic compound as other solvents mixed with BL, and which consist of a kind at least.

[0074] A hypoviscosity solvent may also be included below 20 volume % from a viewpoint in which solvent viscosity is furthermore reduced. As a hypoviscosity solvent, for example, chain-like carbonate, the chain-like ether, cyclic ether, etc. are mentioned.

[0075] The more desirable presentation of a non-aqueous solvent is BL, EC, and PC and VC. [ BL, PC, BL and EC, DEC BL and EC, MEC, BL and EC, MEC, VC and BL, EC, VC and BL, PC and VC or ] [ BL, EC, ] As

for the rate of a volume ratio of EC, at this time, it is desirable to consider as five to 40 volume %. This is based on the following reasons. Since there is a possibility that it may become difficult to cover a negative-electrode front face precisely by the protective coat when the ratio of EC is made under into 5 volume %, the reaction of a negative electrode and BL may arise and it may become difficult to fully improve a charge-and-discharge cycle property. On the other hand, since there is a possibility that the viscosity of nonaqueous electrolyte may become high and ionic conductivity may fall when the ratio of EC exceeds 40 volume %, it may become difficult to fully improve a charge-and-discharge cycle property, a high current discharge property, and a low-temperature discharge property. The still more desirable range of the ratio of EC is ten to 35 volume %. Moreover, the solvent which consists of at least one kind chosen from DEC, MEC, PC, and VC forms a precise protective coat on the surface of a negative electrode, and makes the operation which reduces the interface impedance of a negative electrode. Especially the addition of this solvent is not limited and is set as an amount which this operation produces. However, when the ratio of at least one kind of solvent chosen from DEC, MEC, PC, and VC in a non-aqueous solvent exceeds 10 volume %, there is a possibility that fully controlling may become difficult about nonaqueous electrolyte carrying out oxidative degradation under hot environments, or the viscosity of nonaqueous electrolyte may become high, and ion conductivity may fall. For this reason, as for the rate of a volume ratio of at least one kind of solvent chosen from DEC, MEC, PC, and VC in a non-aqueous solvent, it is desirable to carry out to below 10 volume %. Furthermore, the desirable rate of a volume ratio is below 2 volume %. Moreover, the lower limit with desirable still more desirable making the lower limit of the rate of a volume ratio into 0.001 volume % is 0.05 volume %.

[0076] Especially and the non-aqueous solvent containing BL, EC, and VC below 95 volume % is desirable than 50 volume %. Since the nonaqueous electrolyte rechargeable battery equipped with the nonaqueous electrolyte containing this non-aqueous solvent and the negative electrode containing the carbonaceous object which carries out occlusion emission of the lithium ion can control that a metal lithium deposits in a negative electrode while being able to reduce the impedance of the interface of a negative electrode sharply, it can improve the charge-and-discharge effectiveness of a negative electrode. Consequently, realizing the outstanding high current discharge property and a longevity life, the generation of gas at the time of elevated-temperature storage can be controlled, and deformation of a sheathing material can be suppressed. Thus, it is guessed that it is what is depended on an operation which is explained below that a negative-electrode property is improved. In said rechargeable battery, the protective film by EC is formed in the front face of said negative electrode, and it is alike, in addition the thin and precise coat by VC is formed. Consequently, since the reaction of BL and a negative electrode is suppressed further, it is thought that the fall of an impedance and deposit prevention of a metal lithium are attained.

[0077] Moreover, although it has the presentation mentioned above as a non-aqueous solvent, instead, and the thing containing BL, EC, and the aromatic compound below 95 volume % may be used than 50 volume %. As said aromatic compound, at least one kind chosen from benzene, toluene, a xylene, a biphenyl, and a terphenyl can be mentioned, for example. EC can adhere on the surface of a negative electrode (for example, thing containing the carbonaceous object which carries out occlusion emission of the lithium ion), can form a protective coat, and can control the reaction of a negative electrode and BL. As for the rate of a volume ratio of EC, at this time, it is desirable to consider as five to 40 volume % for the reason same with having mentioned above. Moreover, the still more desirable range of the ratio of EC is ten to 35 volume %. On the other hand, since it is easy to stick on the surface of a negative electrode (for example, thing containing the carbonaceous object which carries out occlusion emission of the lithium ion) to the benzene ring of said aromatic compound, it can control the reaction of a negative electrode and BL. Therefore, and since the nonaqueous electrolyte containing the non-aqueous solvent containing BL, EC, and the aromatic compound below 95 volume % can fully suppress the reaction of a negative electrode and BL, it can improve the charge-and-discharge cycle property of a rechargeable battery than 50 volume %. As for such a non-aqueous solvent, it is desirable that the solvent which consists of at least one kind chosen from DEC, MEC, PC, TFPC, and VC further is included. Since the reaction of a negative electrode and BL can be further controlled by adding the solvent which consists of at least one kind chosen from DEC, MEC, PC, TFPC, and VC, a charge-and-discharge cycle property can be improved further. Especially, VC is desirable. Especially the addition of the 3rd solvent which consists of at least one kind chosen from an aromatic compound, DEC, MEC and PC, TFPC, and VC is not limited, and is set as an amount which this operation produces. However, when the ratio of said 3rd solvent in a non-aqueous

solvent exceeds 10 volume %, there is a possibility that fully controlling may become difficult about nonaqueous electrolyte carrying out oxidative degradation under hot environments, or the viscosity of nonaqueous electrolyte may become high, and ion conductivity may fall. For this reason, as for the rate of a volume ratio of said 3rd solvent in a non-aqueous solvent, it is desirable to carry out to below 10 volume %. Furthermore, the desirable rate of a volume ratio is below 2 volume %. Moreover, the lower limit with desirable still more desirable making the lower limit of the rate of a volume ratio into 0.001 volume % is 0.05 volume %. [0078] As for the amount of dissolutions to said electrolytic non-aqueous solvent, it is desirable to carry out in 0.5-2.0 mols/l.

[0079] In nonaqueous electrolyte, in order [ with a separator ] to be smeared and to improve a sex, surfactants, such as trioctylphosphate, may be added in 0.1 - 1% of range.

[0080] As for the amount of nonaqueous electrolyte, it is desirable to make it per [ 0.2-0.6g ] cell unit capacity 100mAh. This is based on the following reasons. When the amount of nonaqueous electrolysis is set to 0.2g / less than 100 mAhs, there is a possibility that it may become impossible to fully maintain the ionic conductivity of a positive electrode and a negative electrode. On the other hand, when the amount of nonaqueous electrolyte exceeds 0.6g/100mAh, there is a possibility that the amount of electrolytic solutions may become abundant and the closure by the sheathing material made from a film may become difficult. The more desirable range of the amount of nonaqueous electrolyte is 0.4-0.55g/100mAh.

[0081] 5) As for the macromolecule which has the macromolecule aforementioned adhesive property which has an adhesive property, it is desirable that it is what can maintain a high adhesive property where nonaqueous electrolyte is held. Furthermore, when this giant molecule has high lithium ion conductivity, in addition, it is desirable. Specifically, a polyacrylonitrile (PAN), polyacrylate (PMMA), polyvinylidene fluoride (PVdF), a polyvinyl chloride (PVC), or polyethylene oxide (PEO) can be mentioned. Especially, polyvinylidene fluoride is desirable. Polyvinylidene fluoride can hold nonaqueous electrolyte, and since it will produce gelation in part if it contains nonaqueous electrolyte, it can improve ionic conductivity more.

[0082] As for the macromolecule which has an adhesive property, it is desirable to take the vesicular structure which has a detailed hole in a positive electrode, a negative electrode, and the opening of a separator. The macromolecule which has the adhesive property which has a vesicular structure can hold nonaqueous electrolyte.

[0083] As for the total amount of the macromolecule which has the adhesive property included in a cell, it is desirable to make it 0.1-6mg per cell capacity 100mAh. This is based on the following reasons. When the total amount of the macromolecule which has an adhesive property is set to less than 0.1mg per cell capacity 100mAh, there is a possibility that it may become difficult to fully raise the adhesion of a positive electrode, a separator, and a negative electrode. On the other hand, when said total amount exceeds 6mg per cell capacity 100mAh, there is a possibility of causing the fall of the lithium ion conductivity of a rechargeable battery and the rise of internal resistance, and there is a possibility that it may become difficult to improve discharge capacity, a high current discharge property, and a charge-and-discharge cycle property. The more desirable range of the total amount of the macromolecule which has an adhesive property is 0.2-1mg per cell capacity 100mAh.

[0084] 6) It is desirable that the thickness containing a resin layer uses a sheet 0.5mm or less for a sheathing-material sheathing material. Since it has the flexibility (flexibility) of what can make energy density per cell weight high since it is lightweight, this sheathing material is easy to deform by the gas which occurs from an electrode group or nonaqueous electrolyte.

[0085] The resin layer contained in the 1st sheathing material can be formed from polyethylene, polypropylene, etc. It is desirable to arrange a resin layer at the front rear face of the metal layer which makes the role which intercepts moisture preferably, and this metal layer, and to use the unified sheathing material for it.

[0086] \*\*\*\* can mention aluminum, stainless steel, iron, copper, nickel, etc. Aluminum with the function it is lightweight and high especially, which intercepts moisture is desirable. Although said metal layer may be formed from one kind of metal, it may be formed from the thing which made two or more kinds of metal layers unify. The resin layer which touches the exterior among the resin layers arranged at metal \*\*\*\*\* makes the role which prevents damage on said metal layer. This external protective layer is formed from one kind of resin layer, or two or more kinds of resin layers. On the other hand, an internal resin layer bears the role which prevents that said metal layer is corroded by nonaqueous electrolyte. This internal resin layer is formed from

one kind of resin layer, or two or more kinds of resin layers. Moreover, thermal melting arrival nature resin can be arranged on the front face of this internal resin layer.

[0087] If the thickness of a sheathing material exceeds 0.5mm, the capacity per weight of a cell will fall. It is 0.25mm or less to make it 0.3mm or less desirable still more preferably, and the thickness of the 1st sheathing material is 0.15mm or less most preferably. moreover -- if thickness is thinner than 0.05mm -- deformation -- it becomes easy to damage. For this reason, as for the lower limit of thickness, it is desirable to make it 0.05mm. Furthermore, a desirable lower limit is 0.08mm and the most desirable range is 0.1mm.

[0088] The thickness of a sheathing material is measured by the approach explained below. That is, in the field except the closure section of a sheathing material, mutually, it separates 1cm or more, and three existing points are chosen as arbitration, the thickness of each point is measured, and the average is computed, and let this value be the thickness of a sheathing material. In addition, when the foreign matter (for example, resin) has adhered to the front face of said sheathing material, thickness is measured after removing this foreign matter. For example, measurement of thickness is performed after removing PVdF by wiping off the front face of said sheathing material with a dimethylformamide solution, when PVdF has adhered to the front face of said sheathing material.

[0089] As for the rechargeable battery of this invention formed from such each configuration, it is desirable for the products of cell capacity (Ah) and 1kHz cell internal impedance (mohms) to be below 110mohm and Ah more than 10m ohm-Ah. By making the product of capacity and an impedance into said within the limits, a high current discharge property and a charge-and-discharge cycle property can be improved more. Here, cell capacity is the discharge capacity at the time of discharging by nominal capacity or 0.2C. More desirable range is below 60mohm and Ah more than 20mohm and Ah.

[0090] Making the product of cell capacity and an impedance below into 110m ohm-Ah more than 10m ohm-Ah is manufactured by the following manufacture approaches, for example.

[0091] The 1st process: Make a porosity sheet intervene as a separator between the production positive electrode of an electrode group, and a negative electrode, and produce an electrode group.

[0092] After an electrode group winds a positive electrode and a negative electrode around a curled form through macromolecule the separator which is not held [ which has an adhesive property in the meantime ] or winds them around a curled form, it is desirable to compress in the direction of a path or to produce a positive electrode and a negative electrode by bending an adhesive property two or more times in the meantime through macromolecule the non-held separator which it has. It can prevent that said solution permeates the boundary of a positive electrode and a separator, and the whole boundary of a negative electrode and a separator, making the solution of the macromolecule which has an adhesive property in a positive electrode, a negative electrode, and a separator permeate in the 2nd process mentioned later, when it produces by such approach. Consequently, while it becomes possible for you to make it dotted with the macromolecule which has an adhesive property in a positive electrode, a negative electrode, and a separator, the boundary of a positive electrode and a separator and the boundary of a negative electrode and a separator can be made dotted with the macromolecule which has an adhesive property. A positive electrode suspends an electric conduction agent and a binder in positive active material at a suitable solvent, and is produced by applying this suspended solid to a charge collector, drying, and making it the shape of sheet metal. The column of (1) positive electrode mentioned above having explained as said positive active material, an electric conduction agent, a binder, and a charge collector and the same thing can be mentioned. Said negative electrode applies the suspended solid which kneaded the lithium ion under existence of a solvent and was obtained [ lithium ion ] in occlusion, the carbonaceous object to emit, and the binder to a charge collector, and after drying, it is produced by pressing or 2 - 5 times multistage story pressing once by the desired pressure. The column of (2) negative electrodes mentioned above having explained as said carbonaceous object, a binder, and a charge collector and the same thing can be mentioned. The column of (3) separators mentioned above having explained as a porosity sheet of said separator and the same thing can be used.

[0093] The 2nd process: In the sheathing material processed into the insertion saccate to a sheathing material, contain said electrode group so that a laminating side may be in sight from opening. The solution obtained by dissolving the macromolecule which has an adhesive property in a solvent is poured into the electrode group in said sheathing material from opening, and said solution is infiltrated into said electrode group. Said column of (6) sheathing materials mentioned above if the sheathing material's was carried out having explained, and the

same thing can be mentioned. The column of a macromolecule which has the adhesive property of (5) mentioned above as a macromolecule which has said adhesive property having explained, and the same thing can be mentioned. Especially, PVdF is desirable. It is desirable for the boiling point to use an organic solvent 200 degrees C or less for said solvent. this organic solvent -- carrying out -- for example, dimethyl formamide (153 degrees C of boiling points) can be mentioned. When the boiling point of an organic solvent exceeded 200 degrees C and temperature of the vacuum drying mentioned later is made into 100 degrees C or less, there is a possibility that the drying time may start for a long time. Moreover, as for the lower limit of the boiling point of an organic solvent, it is desirable to make it 50 degrees C. When the boiling point of an organic solvent is made into less than 50 degrees C, while pouring said solution into the electrode group, a possibility that said organic solvent may evaporate is. As for the upper limit of the boiling point, it is still more desirable to make it 180 degrees C, and, as for the lower limit of the boiling point, it is still more desirable to make it 100 degrees C. As for the concentration of the macromolecule which has an adhesive property in said solution, it is desirable to make it 0.05 - 2.5% of the weight of the range. This is based on the following reasons. When said concentration is carried out to less than 0.05% of the weight, there is a possibility that it may become difficult to paste up a forward negative electrode and a separator by sufficient reinforcement. On the other hand, when said concentration exceeds 2.5 % of the weight, there is a possibility that it may become difficult to obtain sufficient porosity which can hold nonaqueous electrolyte, and the interface impedance of an electrode may become remarkably large. Increase of an interface impedance reduces capacity and a high current discharge property sharply. The more desirable range of concentration is 0.1 - 1.5 % of the weight. When the concentration of the macromolecule which has the adhesive property of said solution is 0.05 - 2.5 % of the weight, as for the injection rate of said solution, it is desirable to make it the range which is 0.1-2ml per cell capacity 100mAh. This is based on the following reasons. When said injection rate is set to less than 0.1ml, there is a possibility that it may become difficult to fully raise the adhesion of a positive electrode, a negative electrode, and a separator. On the other hand, when said injection rate exceeds 2ml, there is a possibility of causing the fall of the lithium ion conductivity of a rechargeable battery and the rise of internal resistance, and there is a possibility that it may become difficult to improve discharge capacity, a high current discharge property, and a charge-and-discharge cycle property. The more desirable range of said injection rate is 0.15-1ml per cell capacity 100mAh.

[0094] The 3rd process: Evaporate the solvent in said solution and make the macromolecule which has an adhesive property in said positive electrode, a negative electrode, and the opening of a separator exist by performing a vacuum drying to a desiccation electrode group. While pasting up with the macromolecule which has the adhesive property with which these interior and boundaries are dotted with said positive electrode and said separator according to this process, it pastes up with the macromolecule which has the adhesive property with which these interior and boundaries are dotted with said negative electrode and said separator. Moreover, the moisture contained by this vacuum drying in said electrode group is removable to coincidence.

[0095] In addition, an electrode group permits that the solvent of a minute amount is included.

[0096] As for a vacuum drying, it is desirable to carry out below 100 degrees C. This is based on the following reasons. When the temperature of a vacuum drying exceeds 100 degrees C, there is a possibility that said separator may carry out a heat shrink sharply. If a heat shrink becomes large, since a separator will curve, it becomes difficult to paste up a positive electrode, a negative electrode, and a separator firmly. Moreover, when using the porosity film containing polyethylene or polypropylene as a separator, it is easy to produce the heat shrink mentioned above notably. Although the heat shrink of a separator can be controlled so that the temperature of a vacuum drying becomes low, when temperature of a vacuum drying is made into less than 40 degrees C, there is a possibility that it may become difficult to fully evaporate a solvent. For this reason, as for vacuum-drying temperature, it is more desirable to make it 40-100 degrees C.

[0097] The 4th process: Assemble a thin nonaqueous electrolyte rechargeable battery by closing opening of said sheathing material after pouring nonaqueous electrolyte into the electrode group in a closure sheathing material.

[0098] What was explained in the column of (4) nonaqueous electrolyte mentioned above as nonaqueous electrolyte, and the same thing can be used.

[0099] In the manufacture approach mentioned above, although impregnation of the solution in which the macromolecule which has an adhesive property was dissolved was performed after containing the electrode group to the sheathing material, you may pour in, without containing to a sheathing material. In this case, first, a



separator is made to intervene between a positive electrode and a negative electrode, and an electrode group is produced. After infiltrating said solution into said electrode group, the solvent of said solution is evaporated and the macromolecule which has an adhesive property in said positive electrode, a negative electrode, and the opening of a separator is made to exist by performing a vacuum drying to said electrode group. After containing such an electrode group to a sheathing material, nonaqueous electrolyte is poured in and a thin nonaqueous electrolyte rechargeable battery can be manufactured by performing obturation etc. Adhesives may be applied to an electrode group periphery before the receipt to a sheathing material. Thereby, an electrode group can be pasted up on a sheathing material. Moreover, a metal can can be used instead of a film as a sheathing material in this case.

[0100] The 5th process: Perform an initial charge to the assembled rechargeable battery under 30 degrees C - 80 degrees C temperature conditions like the initial charge above at the charge rate of 0.05 or more C and 0.5 C or less. Charge on this condition is good only 1 cycle, and good in a line more than a two cycle. Moreover, you may keep it under a 30 degrees C - 80 degrees C temperature condition before an initial charge for 1 hour to about 20 hours.

[0101] Here, 1C charge rate is a current value required in order to charge nominal capacity (Ah) in 1 hour.

[0102] Specifying the temperature of an initial charge in said range is based on the following reasons. Since the viscosity of nonaqueous electrolyte is still high in initial charge temperature being less than 30 degrees C, it becomes difficult to infiltrate nonaqueous electrolyte into homogeneity to a positive electrode, a negative electrode, and a separator, internal impedance increases, and the utilization factor of an active material falls. On the other hand, if initial charge temperature exceeds 80 degrees C, the binder contained in a positive electrode and a negative electrode will deteriorate.

[0103] Since expansion of the positive electrode by charge and a negative electrode can be moderately made late by making the charge rate of an initial charge into the range of 0.05-0.5C, nonaqueous electrolyte can be made to permeate a positive electrode and a negative electrode at homogeneity.

[0104] Since nonaqueous electrolyte can be infiltrated into the opening of an electrode or a separator by providing such a process at homogeneity, internal impedance which is 1kHz of a nonaqueous electrolyte rechargeable battery can be made small, and the product of 1kHz internal impedance can be carried out to cell capacity in the range below 110m ohm-Ah more than 10m ohm-Ah. Consequently, since the utilization factor of an active material can be increased, capacity of a substantial cell can be enlarged. Moreover, the charge-and-discharge cycle property and high current discharge property of a cell can be raised.

[0105]

[Example] Hereafter, the desirable example of this invention is explained to a detail.

[0106] The example 1 <production of positive active material> mean particle diameter of 3 micrometers and 90% or more of a particle are within the limits of  $\pm 20\%$  of mean particle diameter, the lithium-hydroxide powder whose specific surface area is 30m<sup>2</sup>/g, and the nickel hydroxide powder (nickel<sub>0.75</sub>Co<sub>0.19</sub>aluminum<sub>0.06</sub>(OH)<sub>2</sub>) which carried out the same configuration were prepared, the lithium-hydroxide:nickel hydroxide was fed into the distributed machine with the organic solvent by the ratio of 1.01:1, and the mixed powder which carried out homogeneity distribution was obtained.

[0107] After carrying out temporary baking at 500 degrees C for 2 hours, arranging mixed powder in a firing furnace and making oxygen gas flow in a furnace, after drying mixed powder, this baking was performed at 750 more degrees C for 24 hours, and LixNi<sub>0.75</sub>Co<sub>0.19</sub>aluminum<sub>0.06</sub>O<sub>2</sub> with a mean particle diameter of 10 micrometers was produced. The pH value, average pole diameter, and porosity of the obtained positive-active-material powder are shown in Table 1.

[0108] 91 % of the weight of positive-active-material powder <production of a positive electrode> Obtained 3.5 % of the weight of acetylene black, Add [ both ] 3.5 % of the weight of graphite, 2 % of the weight of ethylene propylene dien monomer powder, and toluene, and it mixes. After applying to both sides of the charge collector which consists of porosity aluminium foil (thickness is 15 micrometers) with which 10cm of holes with a diameter of 0.5mm exists at a rate of ten per two, the electrode consistency produced the positive electrode of the structure where the positive-electrode layer was supported with 2.9 g/cm<sup>3</sup> by both sides of a charge collector, by pressing.

[0109] The powder of a mesophase pitch based carbon fiber (carbonaceous object 20 micrometers and whose average spacing (d<sub>002</sub>) 8 micrometers and mean fiber length are 0.3360nm for the diameter of fiber) heat-

treated at 3000 degrees C as a <production of negative electrode> negative-electrode active material 93 % of the weight, 7 % of the weight (PVdF) of polyvinylidene fluorides is mixed as a binder. The electrode consistency produced the negative electrode of the structure where the negative-electrode layer was supported with 1.4 g/cm<sup>3</sup> by the charge collector, by applying this to the charge collector which consists of porosity copper foil (thickness is 15 micrometers) in which 10cm of holes with a diameter of 0.5mm exists at a rate of ten per two, and drying and pressing it in it.

[0110] 16 micrometers, 120 degrees C, and a heat shrink in 1 hour prepared [ <separator> thickness ] the separator which consists of a porosity film made from polyethylene whose porosity is 50% at 20%.

[0111] <Preparation of nonaqueous electrolyte> 4 lithium borate fluoride (LiBF<sub>4</sub>) was dissolved in the mixed solvent (rate 25:75 of a mixed volume ratio) of ethylene carbonate (EC) and gamma-butyrolactone (BL) 1.5 mols / l, and nonaqueous electrolyte was prepared.

[0112] After welding the band-like positive-electrode lead to the charge collector of the positive electrode obtained by [ as having carried out the <production of electrode group> above-mentioned ], and welding a band-like negative-electrode lead to the charge collector of a negative electrode similarly and winding a positive electrode and a negative electrode around a curled form through said separator between them, it fabricated in the shape of flat, and the electrode group was produced.

[0113] The laminate film with a thickness of 100 micrometers which covered both sides of <assembly of cell> aluminium foil with polypropylene was fabricated to saccate, and this was made into the sheathing material. It contained so that a laminating side might be visible to this sheathing material from opening in a bag in said electrode group. The polyvinylidene fluoride (PVdF) which is the giant molecule which has an adhesive property was dissolved in the dimethyl formamide (the boiling point is 153 degrees C) which is an organic solvent 0.3% of the weight. While the obtained solution is poured in so that the amount per cell capacity 100mAh may be set to 0.2ml at the electrode group in said laminate film, and making said solution permeate the interior of said electrode group, it was made to adhere to the whole front face of said electrode group.

[0114] Subsequently, said organic solvent was evaporated by performing a vacuum drying to the electrode group in said laminate film at 80 degrees C for 12 hours, and porosity jointing was formed in the front face of said electrode group while making the macromolecule which has an adhesive property in the opening of a positive electrode, a negative electrode, and a separator hold. The total amount of PVdF was 0.6mg per cell capacity 100mAh.

[0115] It pours into the electrode group in said laminate film so that the amount per cell capacity 1Ah may be set to 4.7g in said nonaqueous electrolyte, and it has drawing 1 mentioned above and the structure shown in 2, and thickness assembled the thin nonaqueous electrolyte rechargeable battery 40mm and whose height 3mm and width of face are 70mm.

[0116] The following measures were taken as an initial charge process to this nonaqueous electrolyte rechargeable battery. First, after leaving 5h under 40-degree C hot environments, constant current and constant-potential charge were performed to 4.2V by 0.2C (160mA) under the environment for 10 hours. It discharged to 2.7V by 0.2C after that, and charged on the conditions as 1 cycle eye also with the still more nearly same two-cycle eye, and the nonaqueous electrolyte rechargeable battery was manufactured.

[0117] <Characterization> In order to investigate the capacity and the charge-and-discharge cycle property of a non-aqueous-solvent rechargeable battery which were acquired, the capacity maintenance factor after repeating the cycle of 3-hour charge of the 4.2V constant current and the constant voltage in a 0.5C rate and 2.7V discharge of 1C rate and using 300 cycles was measured. Moreover, bulging after high temperature storage of 10 hours was measured at 90 degrees C after 4.2V charge. The cell property of the cell of an example 1 is shown in Table 1. In addition, hereafter, when the amount of bulging was less than 3% of initial thickness, as for O and less than 10% 3% or more of case, O and less than 20% 10% or more of case wrote \*\* and 20% or more of case by x at bulging after 90-degree-C storage of front Naka. Moreover, hereafter, with the capacity recovery factor after 90-degree-C storage of front Naka, when a recovery factor was 95% or more, as for O and less than 95% 90% or more of case, O and less than 90% 75% or more of case wrote \*\* and less than 75% of case by x.

[0118] In the production process of example 2 - example 5 positive active material, except for having changed the ratio of a lithium hydroxide and a nickel hydroxide, the positive active material of pH 10-11.5 was produced like the example 1, the non-aqueous-solvent rechargeable battery was produced like the example 1 using each



obtained positive active material, and cell evaluation was performed still like the example 1. The pH value and cell property of positive active material which were then acquired are shown in Table 1.

[0119] In the production process of example 1 of comparison - example of comparison 4 positive active material, except for having changed the ratio of a lithium hydroxide and a nickel hydroxide, positive active material was produced like the example 1, and the positive active material of pH 10-11.5 which becomes out of range was obtained. The non-aqueous-solvent rechargeable battery was produced like the example 1 using each obtained positive active material, and cell evaluation was performed still like the example 1. The pH value and cell property of positive active material which were then acquired are shown in Table 1.

[Table 1]

|       | 正極活物質<br>pH | 容量<br>(Ah) | 使用後<br>容量維持率<br>(%) | 90°C貯蔵後<br>膨れ | 90°C貯蔵後<br>容量回復率 |
|-------|-------------|------------|---------------------|---------------|------------------|
| 実施例 1 | 11.2        | 1.00       | 92                  | ◎             | ◎                |
| 実施例 2 | 10.0        | 0.95       | 85                  | ○             | ○                |
| 実施例 3 | 10.5        | 0.97       | 85                  | ◎             | ◎                |
| 実施例 4 | 11.0        | 1.00       | 90                  | ◎             | ◎                |
| 実施例 5 | 11.5        | 1.00       | 90                  | ○             | ○                |
| 実施例 6 | 11.2        | 1.00       | 92                  | ◎             | ◎                |
| 比較例 1 | 9.0         | 0.85       | 80                  | ×             | ×                |
| 比較例 2 | 9.5         | 0.85       | 82                  | △             | △                |
| 比較例 3 | 11.7        | 1.05       | 82                  | △             | △                |
| 比較例 4 | 12.0        | 1.10       | 80                  | ×             | ×                |

Except for having changed the particle size of the raw material powder at the time of producing example 6 - example 9 positive active material, positive active material was produced like the example 1, and the positive active material whose average pole diameter is 3nm - 30nm was produced. The non-aqueous-solvent rechargeable battery was produced like the example 1 using each obtained positive active material, and cell evaluation was performed still like the example 1. The average pole diameter and cell property of positive active material which were then acquired are shown in Table 2 with the result of an example 1.

[0120] Except for having changed the particle size of the raw material powder at the time of producing the example 5 of a comparison, and 6 positive active material, positive active material was produced like the example 1, and the positive active material out of range whose average pole diameter is 3nm - 30nm was produced. The non-aqueous-solvent rechargeable battery was produced like the example 1 using each obtained positive active material, and cell evaluation was performed still like the example 1. The average pole diameter and cell property of positive active material which were then acquired are shown in Table 2 with the result of an example 1.

[Table 2]

|       | 正極活物質<br>pH | 平均<br>細孔径<br>(nm) | 容量<br>(Ah) | 使用後<br>容量維持率<br>(%) | 90°C貯蔵後<br>膨れ | 90°C貯蔵後<br>容量回復率 |
|-------|-------------|-------------------|------------|---------------------|---------------|------------------|
| 実施例 1 | 11.2        | 18                | 1.00       | 92                  | ◎             | ◎                |
| 実施例 6 | 11.2        | 3                 | 1.05       | 89                  | ◎             | ◎                |
| 実施例 7 | 11.2        | 10                | 1.02       | 90                  | ◎             | ◎                |
| 実施例 8 | 11.2        | 20                | 1.00       | 92                  | ◎             | ◎                |
| 実施例 9 | 11.2        | 30                | 0.98       | 93                  | ◎             | ◎                |
| 比較例 5 | 11.2        | 1                 | 1.00       | 80                  | ○             | ○                |
| 比較例 6 | 11.2        | 50                | 0.90       | 93                  | ○             | ○                |

Except for having changed the temperature of this baking at the time of producing example 10 - example 13 positive active material, positive active material was produced like the example 1, and pore volume 0.01 cc/g-0.1cc/g positive active material was obtained. The non-aqueous-solvent rechargeable battery was produced like

the example 1 using each obtained positive active material, and cell evaluation was performed still like the example 1. The average pore diameter and cell property of positive active material which were then acquired are shown in Table 3 with the result of an example 1.

[0121] Except for having changed the temperature of this baking at the time of producing the example 7 of a comparison, and 8 positive active material, positive active material was produced like the example 1, and the positive active material which has pore volume out of range [ 0.01cc/g - 0.1 cc/g ] was obtained. The non-aqueous-solvent rechargeable battery was produced like the example 1 using each obtained positive active material, and cell evaluation was performed still like the example 1. The average pore diameter and cell property of positive active material which were then acquired are shown in Table 3 with the result of an example 1.

[Table 3]

|        | 正極活物質<br>pH | 細孔容積<br>(cc/g) | 容量<br>(Ah) | 使用後<br>容量維持率<br>(%) | 90°C貯蔵後<br>膨れ | 90°C貯蔵後<br>容量回復率 |
|--------|-------------|----------------|------------|---------------------|---------------|------------------|
| 実施例 1  | 11.2        | 0.0070         | 1.00       | 92                  | ◎             | ◎                |
| 実施例 10 | 11.2        | 0.0010         | 1.05       | 89                  | ◎             | ◎                |
| 実施例 11 | 11.2        | 0.0030         | 1.02       | 90                  | ◎             | ◎                |
| 実施例 12 | 11.2        | 0.0050         | 1.00       | 91                  | ◎             | ◎                |
| 実施例 13 | 11.2        | 0.0100         | 0.98       | 92                  | ◎             | ◎                |
| 比較例 7  | 11.2        | 0.0005         | 1.00       | 79                  | ○             | ○                |
| 比較例 8  | 11.2        | 0.0300         | 0.90       | 92                  | ○             | ○                |

As mentioned above, when pH of positive active material was controlled within the limits of 10.5-11.5 to be shown in Table 3 from Table 1, it turned out that cell bulging at the time of elevated-temperature storage is controlled effectively. Moreover, when the pore pitch diameter of positive active material was controlled to 3-30nm and the highest volume was controlled within the limits of 0.001 - 0.01 cc/g, it turned out that cell bulging is controlled further.

[0122]

[Effect of the Invention] As explained in full detail above, according to this invention, deformation of the sheathing material at the time of storing at an elevated temperature is controlled, and the nonaqueous electrolyte cell which has the charge-and-discharge cycle property excellent in high capacity can be offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The sectional view showing an example of the nonaqueous electrolyte cell of this invention.

[Drawing 2] The expanded sectional view showing the A section of drawing 1.

[Drawing 3] The mimetic diagram showing the positive electrode in the nonaqueous electrolyte cell of drawing 1, a separator, and near the boundary of a negative electrode.

[Description of Notations]

- 1 -- Sheathing material
- 2 -- Electrode group
- 3 -- Separator
- 4 -- Positive-electrode layer
- 5 -- Positive-electrode charge collector
- 6 -- Negative-electrode layer
- 7 -- Negative-electrode charge collector
- 8 -- Glue line
- 9 -- Macromolecule which has an adhesive property
- 12 -- Positive electrode
- 13 -- Negative electrode

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[Translation done.]

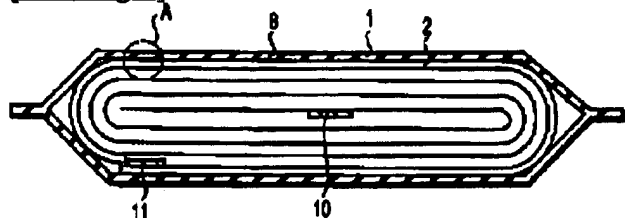
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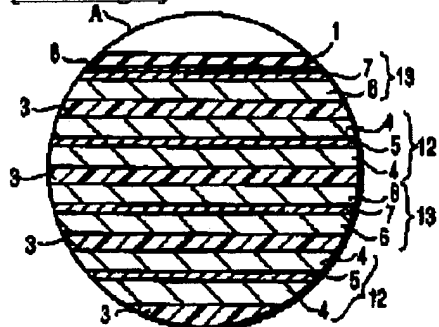
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## DRAWINGS

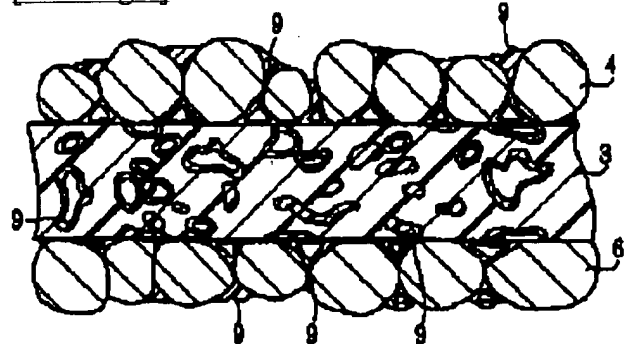
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]